"Development of Metal Titanate ($NiTiO_3$, $MnTiO_3$) Electrodes for Electrochemical Supercapacitor Applications"

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Ph.D. Synopsis / Work Plan

Proposed Title: Development of Metal Titanate ($NiTiO_3$, $MnTiO_3$) Electrodes for Electrochemical Supercapacitor Applications

Abstract of proposed work plan/problem:

Supercapacitors are emerging as promising energy storage devices due to their high-power density, rapid charge-discharge cycles, and long cycle life. This proposed work plan outlines a comprehensive research initiative aimed at advancing the field of supercapacitor technology through the development and characterization of metal titanate electrodes, specifically focusing on $NiTiO_3$ and $MnTiO_3$. Metal titanates, with their unique electrochemical properties, present an opportunity to enhance the performance of supercapacitor electrodes. Structural, morphological, compositional, optical, and electrical properties of Metal Titanate ($NiTiO_3$ and $MnTiO_3$) thin films will be studied by using XRD, SEM, FESEM, EDAX, UV–Vis spectroscopy, DC electrical conductivity measurement. The electrochemical measurements such as cyclic voltammograms, galvanostatic charge/discharge and electrochemical impedance spectroscopy measurements will be carried out to study the supercapacitor performance of the Metal Titanate ($NiTiO_3$ and $MnTiO_3$) electrodes.

1.Introduction:

Significant development in the field of renewable energy technologies such as solar cells and fuel cells is going on. In the past, these types of energy sources have been marginalized, but as new technology makes substitute energy more practical and price competitive with fossil fuels, it is expected that the coming decades will show a long-expected transition away from oil and gasoline as our primary fuel. Although a variety of renewable energy technologies as well as new storage devices have been developed, they have not reached wide-spread use. Therefore, there is a strong need of development of improved methods for storing energy when it is available and retrieving when it is needed. In the ever-evolving landscape of energy storage technologies, supercapacitors have garnered significant attention for their ability to deliver high-power density, rapid charge-discharge cycles, and extended operational lifetimes. Supercapacitors are being developed as an alternative to pulse batteries. In general, for a particular set of materials, a sacrifice in energy density is required to get a large reduction in the time constant and thus a large increase in power capability [1].

The electrochemical capacitors (ECs) or supercapacitors (SCs) represent a new generation of electrochemical energy storage components with very high capacitance for energy storage. Supercapacitors store energy in either capacitive (double layer of electrostatic charges) or pseudocapacitive (a faradic battery-like reaction) nature. Exploiting both the advantages of battery (high energy density) and conventional capacitors (high power density), supercapacitors easily offer higher specific capacitance values up to several thousand farad for applications requiring pulse power. Being an independent existence of supercapacitors, hybrid capacitors have more to render in terms of power and energy [2]. This class of energy storage device which bridge the gap between traditional capacitors and batteries is commonly known in many names such as supercapacitor (SC).

The choice of electrode materials plays a pivotal role in determining the overall performance of supercapacitors. The quest for materials that can enhance the performance of supercapacitor electrodes has led to a focus on metal titanates, with specific emphasis on Nickel Titanate ($NiTiO_3$) and Manganese Titanate ($MnTiO_3$). These metal titanates exhibit unique electrochemical properties, making them promising candidates for advancing supercapacitor technology. This proposed work plan aims to undertake a systematic investigation into the synthesis, characterization, and application of $NiTiO_3$ and $MnTiO_3$ as electrode materials for supercapacitors. The rationale behind this research lies in the potential to exploit the favorable attributes of metal titanates, such as their high conductivity, structural stability, electrochemical reactivity, unique crystal structures and electronic configurations to develop electrodes with enhanced energy storage and charge-discharge capabilities. However, a comprehensive understanding of their potential as supercapacitor electrodes, including their synthesis, structural optimization, and electrochemical performance, is yet to be fully explored. The successful development of $NiTiO_3$ and $MnTiO_3$ electrodes holds significant promise for addressing the growing energy storage needs across various sectors.

The proposed work plan adopts a systematic approach to realize the objectives outlined. Beginning with a thorough literature review to understand the current state of knowledge, the research will delve into the synthesis of $NiTiO_3$ and $MnTiO_3$ using various chemical methods. The synthesized materials will then undergo rigorous characterization using advanced techniques such as X-ray diffraction (XRD) and scanning electron microscopy (SEM) to analyze their structural and morphological features. Following successful synthesis and characterization, the research will progress to the fabrication of supercapacitor electrodes using the optimized $NiTiO_3$ and $MnTiO_3$ materials. Electrochemical performance evaluation including cyclic voltammetry, galvanostatic charge-discharge cycling, and impedance

spectroscopy, will provide crucial insights into the specific capacitance, stability, and overall suitability of the metal titanates as supercapacitor electrodes.

2. Review of Literature and Development in the Subject (Previous work done in the relevant area):

Penetrating into the current market as a feasible alternative to batteries, supercapacitors are paving ways for researchers to investigate all possible materials that could deliver enhanced performances in terms of power and energy density, charge-discharge characteristics, cycling stability and reversibility [2].

Electrical capacitance of supercapacitors is quite dependent on the number of ions present at the electrode/electrolyte interface. Highly increased specific surface area of these new electrode materials is essential for the supercapacitors to obtain remarkably increased number of ions adsorbed on the surface of electrodes so as to realize the so-called "supercapacitance". The charge time becomes very rapid up to a few seconds and the specific power density is at least two orders higher than the secondary or rechargeable batteries [1, 2].

When metal oxides and carbon composite conducting polymer are used as electrodes for the construction of EDLCs, the charge storage mechanism includes both double layer capacitance and pseudo capacitance which result in higher capacitance output and the EDLCs are termed as supercapacitors (SCs). One major disadvantage of carbon based EDLC is the lower specific stored energy. Metal oxides are attractive alternative to an electrode material because of high specific capacitance at low resistance, possibly making it easier to construct high-energy, high-power supercapacitors. Some of the oxides which have been studied as SC electrode material are NiO, MnO_2, Co_3O_4, IrO_2, SnO_2 and V_2O_5. In the case of redox supercapacitors, various noble and transition metal oxides (e.g., RuO_2, CoO_x, NiO_x, MnO_2, etc.) have been employed as electrode materials [3-7].

Researchers have explored various synthesis methods for metal titanates, including $NiTiO_3$ and $MnTiO_3$. Hydrothermal synthesis, sol-gel process and solid-state methods have been investigated for their ability to control particle size, morphology, and crystallinity.

Weijia Zhou et al. (2014) [8] investigate the impact of introducing nickel ions into the titanate nanowire structure to improve electrochemical performance. Electrochemical studies show that the $K_2Ti_4O_9$@Ni $(OH)_2$/Ti electrodes possess a high specific capacitance of 340 mF/cm^2 at 50 mV/s with an excellent retention rate of 92.5% after 2000 cycles and 92.7% after 10 000 cycles respectively. The enhanced capability of the chemically modified titanate electrodes may open up new opportunities in the development of low-cost, high-performance, and flexible supercapacitors.

LIU Huan-Long et al. (2018) [9] by using Sol-Gel method demonstrated excellent rate performance of $MnTiO_3$@rGO anode, showcasing its ability to maintain a specific capacity of 286 $mAh \cdot g^{-1}$ at 5.0 $A \cdot g^{-1}$, emphasizing its potential for high-power applications. The porous structure and flexible rGO shell further contribute to the anode's long-term cycling stability. The $MnTiO_3$@rGO composite maintains a specific capacity of 441 $mAh \cdot g^{-1}$ after 500 cycles at 0.5 $A \cdot g^{-1}$, with only 8.4% loss, highlighting its remarkable stability and longevity.

Narasimharao Kitchamsetti et al. (2020) [10] presents a comprehensive exploration of mesoporous NTO rods synthesized via the sol-gel route, showcasing their remarkable potential as supercapacitor electrodes. The mesoporous NTO rods, with increased textural boundaries, demonstrate enhanced ion diffusion, contributing to a specific capacitance (Cs) of 542.26 F/g, exceptional energy density of 8.06 Wh/kg and power density of 4320 W/kg are achieved in an aqueous KOH electrolyte, outperforming Ni, Mn, Fe, Cr, and Ti-based perovskites or mixed-phase materials. The diffusion-controlled, easy/faster access to OH^- ions within the rod body, with a short diffusion time of 20.4 µs, results in a long life cycle, high stability up to 2100 cycles, and an impressive retention rate of 91%.

Narasimharao Kitchamsetti and colleagues (2022) [11] reported the ultrathin 2D MTO nanodiscs of $MnTiO_3$ which exhibit notable electrochemical performance metrics, including a specific capacitance of 1513.7 F/g, specific capacity of 103.2 mAh/g, specific power of 1351.9 W/kg, and specific energy of 52.2 Wh/kg. A remarkable 85.1% capacitance retention is observed even after 5000 cycles in a 2 M aqueous KOH electrolyte, indicating outstanding long-term stability.

Debabrata Nandi et al. (2022) [12] showed that the nickel titanate nanosphere-based electrode exhibits remarkable electrochemical performance, boasting a high specific capacitance of 885 F g^{-1} and an energy density of 30.73 Wh kg^{-1}. This performance is achieved without compromising power density, recorded at 124.21 W kg^{-1} at a current density of 0.5 A g^{-1} in a 1 M Na_2SO_4 electrolyte. The stability and rate capability of the supercapacitor are noteworthy, remaining largely unchanged even with a change in current density from 0.5 to 2.5 A g^{-1}. After 10,000 cycles, the supercapacitor exhibits high-rate capability (~82%) and 95% Coulombic efficiency, highlighting its promising stability. The relaxation time of 0.35 s indicates the superior rate performance of the $NiTiO_3$ nanosphere-based supercapacitor, implying the rapid release of stored energy.

Elzbieta Regulska and coworkers (2022) [13] studied the electrochemical performance of the $NiTiO_3$/rGO composite which is evaluated through cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), and galvanostatic charge/discharge measurements (GCD). The composite exhibits outstanding specific capacitance (551 F g^{-1} at 10 mV s^{-1}) and exceptional capacitance retention (121%), underscoring its efficacy as a supercapacitor material. A remarkable power density of 9718 W kg^{-1} (at 20 A g^{-1}) and a significantly reduced charge transfer resistance (56 Ω, 2-fold smaller than bare $NiTiO_3$) further highlight its superior electrochemical behavior.

Subramani Dhinakaran et al. (2024) [14] done GCD analysis of an asymmetric supercapacitor (ASC) using Monoclinic Ni_2ZnMoO_6 Double Perovskites (NZMO DP) as the electrode in 6 M KOH electrolyte at 0.5 A g^{-1} yields a maximum specific capacitance of 160.45 Fg^{-1}. The ASC-NZMO monoclinic DP demonstrates exceptional electrochemical stability, with a specific capacitance retention of 91.37% after 6000 cycles. The asymmetric supercapacitor (ASC) based on monoclinic NZMO DP exhibits an excellent power density of 646.25 W/kg and an energy density of 20.53 Wh/kg, highlighting its potential for practical applications.

3. Objectives of Research / proposed Hypothesis:

- **Synthesis Optimization: -**

- Develop and optimize synthesis methods for metal titanates - $NiTiO_3$ and $MnTiO_3$.
- Investigate different synthesis routes, such as CBD, Electrodeposition, sol-gel, hydrothermal, and solid-state methods to enhance the efficiency and reproducibility of electrode material production.

- **Structural Characterization: -**

- Conduct a detailed structural analysis using techniques like X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), Energy Dispersive Analysis by X-Rays (EDAX) etc. to understand the crystal structure, morphology, composition and electrical properties of $NiTiO_3$ and $MnTiO_3$.
- Explore the correlation between the structural features and electrochemical performance of the electrodes such as cyclic voltammetry and galvanostatic charge/discharge by using various electrolyte solutions.
- Investigate strategies to enhance the electrochemical performance of $NiTiO_3$ and $MnTiO_3$ electrodes, such as surface modification, or hybridization with other materials.

- Explore the impact of different factors such as temperature and electrolyte composition on the performance of the electrodes.

➢ **Understanding Electrochemical Mechanisms: -**

- Investigate the fundamental electrochemical mechanisms governing the charge storage and transfer processes in $NiTiO_3$ and $MnTiO_3$ electrodes.
- Utilize advanced characterization techniques and in-situ analysis to elucidate redox reactions, ion diffusion kinetics, and the stability of active materials during charge-discharge cycles.

4. Methodology to be adopted:

There are several methods in the literature for the synthesis such as Chemical Bath Deposition, Electrodeposition, SILAR, Hydrothermal and Sol-gel which is reliable and easy to synthesis of metal. Among this method, one of the synthesis methods will be used to synthesized metal titanates.

a) Preparation of Good Quality $NiTiO_3$ and $MnTiO_3$ Electrodes.

It is proposed to grow $NiTiO_3$ and $MnTiO_3$ electrodes by chemical methods. At initial stages, the efforts will be done in order to deposit good quality $NiTiO_3$ and $MnTiO_3$ thin films on substrates. The various preparative parameters like concentration of precursor solution, thickness, substrate temperature and other parameters will be optimized to get good quality $NiTiO_3$ and $MnTiO_3$ thin films. The as deposited films will be characterized by various characterization techniques.

b) Structural Studies:

The as deposited $NiTiO_3$ and $MnTiO_3$ thin films will be characterized by X-Ray diffraction (XRD) technique, X-ray photoelectron spectroscopy (XPS), Energy Dispersive Analysis by X-Rays (EDAX). The crystal structure, interplanar spacing, lattice planes, micro strain, dislocation density, number of crystallites per unit area, lattice parameters and crystallite size will be obtained and correlated with the film properties.

c) Morphological and Compositional Studies:

The morphology of the prepared $NiTiO_3$ and $MnTiO_3$ thin films will be studied by using Scanning Electron Microscopy (SEM) or Atomic Force Microscopy (AFM) transmission electron microscopy (TEM), The grain size, surface roughness, porosity will be studied using SEM and AFM techniques. The compositional analysis of as deposited $NiTiO_3$ and $MnTiO_3$ thin films will be studied by using Energy Dispersive Analysis by X-Rays (EDAX) technique. The correlation between as taken composition and film composition will be obtained.

d) Optical Studies:

The optical absorption of $NiTiO_3$ and $MnTiO_3$ thin films will be obtained by using UV–Vis (Ultraviolet–Visible) spectrophotometer. The coefficient of absorption, band gap energy (E_g), nature of transition, power factor will be obtained from optical absorption spectra.

e) Electrical Studies:

The electrical resistivity measurements of as deposited $NiTiO_3$ and $MnTiO_3$ thin films will be carried out by using DC two-point probe method. The room temperature conductivity, activation energy will be obtained and correlated with film properties.

f) Electrochemical Supercapacitor Studies:

Performance of $NiTiO_3$ and $MnTiO_3$ thin films in supercapacitor will be evaluated with respect to various parameters such as scan rate, specific capacitance, stability cycles and potential range. The super capacitive performance of $NiTiO_3$ and $MnTiO_3$ thin films will be tested for symmetric and asymmetric modes, for achieving high power density. The galvanostatic charge-discharge mechanism will be studied using chronopotentiometry and the parameters such as specific capacitance, coulomb efficiency, specific energy, and specific power will be calculated. The electrochemical impedance spectroscopy analysis will be carried out.

g) Effect of technical parameter:

To study the effect of technical parameter, the film thickness will be studied for all above-mentioned characteristics.

The purpose of research work is to improve pseudo-capacitive properties such as specific power, specific energy and coulomb efficiency of $NiTiO_3$ and $MnTiO_3$ thin films.

5. Importance of Study/Society Application:

A modern technological society demands the use and storage of energy on a major scale, employing large and small system for that purpose. The energy stored in the capacitor is nonfaradaic electrical energy. No chemical changes are involved and hence cycle life of capacitor is unlimited. Super capacitors are maintenance free. Now a day's electrochemical capacitors or supercapacitors are used as storage devices to complement batteries. Supercapacitor have attracted more and more attention because of their advantages such as fast charging and discharging, long life span, simple principle and high-power density compared with lithium batteries and traditional dielectric capacitors. Supercapacitors are used in particular cars and trains, light weight electronic fuse, backup power sources for calculators, portable electronic devices, foldable electronic devices and wearable mobile phones.

6. Proposed Work Plan / Formulation and Structure of Study:

Year wise plan of work and target to be achieved:

Plan of Work and Target to be achieved during First Year:

During the first year all chemicals will be procured. A through literature survey will be done in order get good knowledge of metal titanates and supercapacitors. Efforts will be done in order to deposit good quality $NiTiO_3$ and $MnTiO_3$ thin films. Various preparative parameters will be optimized.

Plan of Work and Target to be achieved during Second Year:

In second year the $NiTiO_3$ and $MnTiO_3$ thin films will be characterized by various techniques such as XRD, SEM, FESEM, AFM, TEM and EDAX, in order to study the structural, morphological and compositional properties. The films will be studied for optical properties using UV-Vis spectrophotometer. The as grown films will be characterized by electrical resistivity measurement. The performance of $NiTiO_3$ and $MnTiO_3$ thin films in supercapacitor will be evaluated with respect to various parameters such as scan rate, specific capacitance, stability cycles and potential range. The results obtained will be discussed and interpreted. At least two progress reports will be sent during the year. Two research papers will be communicated to the reputed journal at the end of this year.

Plan of Work and Target to be achieved during Third Year:

Results obtained in second year will be analyzed and published in reputed journals. Also, the outcomes of our research work will be presented in national and international gatherings such as Seminars, Workshops, and Conferences set during this year. Once this is done final synopsis will be submitted and after this thesis will be written. Thesis will be submitted to the university.

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